Optimized manufacturing of thermoplastic biocomposites by fast induction-heated compression moulding: influence of processing parameters on microstructure development and mechanical behaviour

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Abstract

The optimization of processing tools and manufacturing procedures are key issues for the development of high-performance biocomposites materials. In this study, we investigated the manufacturing of commingled flax / polypropylene fabrics by fast induction-heated compression moulding to produce lightweight thermoplastic biocomposites. The processing / microstructure / mechanical behaviour relationships of these biocomposites were established based on a careful microstructural analysis through DSC, pycnometry, SEM and X-ray tomography. Elastic properties of the biocomposites could be maintained even at high processing temperature, but their strength was drastically decreased due to extensive fibre degradation and formation of macro-pores. An optimised set of processing parameters was found for an improved microstructure with limited porosity and fibre degradation. The use of fast induction-heated systems can thus be an interesting solution to overcome the thermal degradation processes occurring with natural fibres reinforced biocomposites, hence opening the doors for the use of higher melting point polymer matrices.

Keywords: A. Biocomposite; B. Mechanical properties; D. Microstructural analysis; E. Compression moulding

1. Introduction

Natural fibres are considered as potential substitute to traditional composite reinforcements due to their low density, high specific mechanical properties, relative worldwide abundance and low cost, and positive environmental profile [1]. Bast fibres such as flax, hemp, kenaf, jute and ramie are extracted from the periphery of the stems, and have a hierarchical structure with bundles of packed elementary fibres built up of a layered cell wall structure, *i.e.* the primary and secondary cell walls [2]. The secondary cell wall, mainly made of cellulose microfibrils as reinforcements and hemicelluloses as a matrix component, is responsible for the high tensile strength and stiffness of elementary fibres, due to high cellulose content and low microfibrillar angle towards the fibre direction. In particular, the specific longitudinal stiffness of flax fibres in tension can even be higher than that of glass fibres due to the lower density of flax [3].

In this regard, bast fibres such as flax are intended to be used in structural composite applications [4]. However, the structural potential of flax fibres as reinforcements in structural composites can only be realized by taking advantage of twistless long fibre yarns, and the study of woven flax fibres reinforced thermoplastic biocomposites is therefore of great interest. There is limited literature on the influence of the type of flax fibres, the typical length of fibres and fabric architecture, the resin system used, and the composite manufacturing process on the mechanical performances of thermoplastic biocomposites. Moreover, it is noteworthy that the composite manufacturing process can be more influential on the final properties of flax fibre reinforced thermoplastic composites than for carbon and glass fibre composites. Indeed, natural fibres used as reinforcement in composites are exposed to high temperatures during composites manufacturing, especially in the case of semi-crystalline thermoplastics matrices that require high processing temperatures for melting and flowing. Liang et al. [5] pointed out that for plant fibre based composites, the choice of manufacturing conditions and thermoplastic matrices are limited by the high melting point of some thermoplastics and the consecutive thermal degradation of natural fibres

at high temperatures, due to the presence of thermally sensitive constituents such as waxes, pectins, hemicelluloses and lignin. Gassan and Bledzki [6] noted that heating of lignocellulosic based materials to temperatures of 100 to 250 °C could cause alterations in either their physical or chemical structures such as depolymerization, hydrolysis, oxidation, dehydration, decarboxylation and recrystallization, which in turn resulted in changes in the physical properties of natural fibres. The thermal degradation of flax fibres is dependent on both the temperature and duration of exposure. For example, prolonged exposure of 2 hours at temperature of 210 °C results in reduction in the tenacity of flax fibres of roughly 70% [6]. Gourier et al. [7] studied the effect of thermal cycles on the mechanical behaviour of elementary flax fibres, and found that modifications in the fibre structure and the interactions between components occur at high temperatures such as 250 °C. In order to minimize fibre damages, Van de Velde and Baetans [8] reported that exposing flax fibres for 15 minutes at 180 °C results in lower residual tensile stress and strain than when exposed for two hours at 120 °C. Based on their results, the authors recommended that composite production temperatures higher than 180 °C should be avoided, unless the processing duration is short.

The thermal degradation of flax fibres then constitutes a strong limitation regarding the development of high performance thermoplastic biocomposites reinforced with natural fibres. Indeed, Bourmaud et al. [9] who studied the effect of the processing temperature on mechanical performances of unidirectional flax fibre reinforced polyamide 11 (PA 11) composites found that a thermal cycle of 8 minutes at 210 °C reduces both the stiffness and strength of the composite. As a consequence, the mechanical performances that can be expected with flax fibres composites are restricted by the use of low melting temperature thermoplastic matrices with limited mechanical properties. For instance, John and Anandjiwala [10] recommended the use of PP as matrix as it requires a relatively low processing temperature. Van de Velde and Kiekens [11] studied the effect of processing parameters, i.e. temperature and time, in a hot-press setup on the mechanical properties of non-woven flax / PP composites, and also recommended a maximum processing temperature of

200 °C to preserve the mechanical properties of flax fibres. Different recommendations regarding exposure of natural fibres to temperature can thus be found in literature and are highly dependent of the residence time and the expectation in terms of physical properties toward the targeted application.

Different strategies have been investigated to preserve the integrity of natural fibres during composite manufacturing, in particular by reducing their exposure time to high temperatures. In this regard, the use of woven commingled fabric made of flax fibres and polypropylene (PP) fibres is one of the solutions that can reduce the thermal degradation of flax fibres during composite fabrication. These woven products are made of hybrid wrap yarn consisting of two components; a yarn core with twist-free staple fibres of flax and PP, and a PP filament wound around the core, limiting defibrillation during weaving and composite manufacturing processes. Further details on the structure of the natural fibre/thermoplastic fibre hybrid yarn and the weaving process using wrap spinning method were given by Baghaei et al. [12] and Zhang and Miao [13]. The main advantage of hybrid yarns containing both matrix and reinforcing components in its structure is that the commingled structure improves the impregnation efficiency by the thermoplastic resin during composite manufacturing due to the lowest effective resin flow distance [14,15]. This was confirmed by Kannan et al. [16] who observed that the interwoven fabric structures provide shorter resin flow time and good matrix impregnation compared to other possible preforms. A comparison of the thermal degradation of flax / PP composite to pure flax and PP yarns showed a positive shift in the degradation temperature of the composite, and it was hypothesized that the improved thermal stability of the composite was due to the good degree of matrix covering the flax yarns, achieved with the interwoven fabric. Furthermore, it was reported that wrap yarn with a twistless natural fibre core wrapped by a PP filament led to composites which demonstrated a significant improvement in flexural modulus over those with conventional twisted yarn structure, in a range of fibre volume fraction ratios [13]. This improvement could be explained by enhanced fibre orientation and

dispersion and better packing of the laminate due to improved resin impregnation during manufacturing.

The manufacturing process used for the consolidation of composites also has a great influence on the thermal degradation of flax fibres. Because of the high processing temperatures required for lowering the matrix viscosity and accelerating the impregnation process, fibre degradation may occur during the heating stage and affect the final properties of composites regardless the consolidation process. Hot press compression moulding is commonly used for the manufacturing of long fibre reinforced thermoplastic composites. Hot presses are efficient systems for applying the high temperatures and pressures that are required for ensuring full consolidation of thermoplastic composites [17][18]. However conventional hot presses with platens equipped with cartridge heaters exhibit limited heating rates, usually below 5 °C/min. Natural fibre degradation can therefore be already well advanced at the isothermal stage. To overcome this problem, Kazmi et al. [19] proposed a vacuum assisted oven consolidation (VAOC) technique. The effect of different pressure and temperature cycles on the consolidation quality of flax / PP composites manufactured using this VAOC technique was investigated and an optimum processing cycle to reduce the manufacturing time without significantly altering the mechanical properties of the laminates was proposed. Another alternative technique for limiting the exposure time of natural fibres and thereby reducing the consequential thermal degradation is the use of a fast heating manufacturing system. Such approach is a key to better control the processing of woven natural fibres reinforced thermoplastic composites and hence reach the mechanical performances expected for structural applications.

In this study, a compression moulding system based on induction technology was used to manufacture consolidated lightweight composites from commingled flax / PP fabrics. This system allows mould heating and cooling kinetics of about 40 °C/min, and hence short compression moulding cycles [20]. The effect of processing conditions on the microstructure and mechanical properties of the biocomposites were studied for a better understanding of their process-

microstructure-property relationships. Accounting of respective thermal properties of flax and PP fibres, flax/PP biocomposite laminates were manufactured with varying and contrasted processing parameters in terms of thermal cycles and applied pressures. Tensile tests were conducted on the resulting biocomposites to determine the influence of the processing conditions on their elastic and ultimate properties.

2. Materials and methods

2.1. Materials

The material chosen for the study was a woven commingled fabric of flax / polypropylene (PP), supplied by Composites Evolution as Biotex flax / PP with surface density of 400 $g.m^{-2}$ and made from twistless flax fibres and PP fibres in a balanced 2 × 2 twill architecture. The biochemical composition of flax was analysed by Fibre Recherche Développement® (FRD, Troyes, France) according to Van Soest method (standards NF EN ISO 13906 and NF V18-122): cellulose (79.6% ± 0.9), hemicelluloses (5.5% ± 0.5), lignin (7.6% ± 0.3), solubles (6.9% ± 0.2) and ashes (0.4% ± 0.1).

2.2. Manufacturing of flax / PP biocomposites

Compression moulding was chosen for the fabrication of the composite laminates because of its high reproducibility and low cycle time [21]. The commingled fabrics were moulded into flax fibre reinforced thermoplastic composite laminates by applying a heating and pressure cycle to melt the PP fibres and impregnate the flax reinforcement, followed by a cooling cycle for the PP crystallisation and consolidation of the laminates. In this study, we used a fast compression moulding system based on induction technology (3iTech® from Roctool). The pilot plant consists in a vertical press of 1000 kN capacity, a 200 kW medium-frequency induction generator, a water cooling unit

that can supply cold water up to 100 L/min and a flat tool of 400 × 400 mm² moulding area (Figure 1).

Eight plies of the flax / PP commingled fabric were cut to 280 × 280 mm², and placed between the two rigid steel plates of the hydraulic press. Based on the supplier datasheet, the initial flax fibre volume fraction of the fabrics was 40% and the estimated consolidated thickness of 0.3-0.35 mm per ply, which corresponds to a theoretical final thickness of the composite laminate of 2.4 mm. The fabrics were pre-dried at 70 °C overnight before composite manufacturing in order to remove the excess moisture.

Figure 1. (a) Fast induction-heated compression moulding press, (b) Close view of flax/PP commingled fabric, (c) 8 plies fabric layup and (d) Manufactured composite laminate.

Composite panels were manufactured by placing the stack of commingled fabrics between the two rigid steel plates of the hydraulic press at room temperature and considering several processing parameters, *i.e.* temperature, pressure and consolidation time, for the manufacturing of the flax / PP composite laminates. All laminates were prepared following a specific thermal/pressure cycle comprised of three main phases: an initial heating period with gentle pressure to ensure a good contact and thermal conduction within the flax/PP commingled fabrics, followed by an isothermal phase during which pressure was applied and molten PP could impregnate flax fibres, and the final cooling phase during which PP crystallization and consolidation of the composite laminates occurred. The operating temperatures were chosen based on the thermal analysis conducted on the flax and PP fibres.

2.3. Thermal properties of polypropylene, flax fibres, and biocomposites

Differential Scanning Calorimetry (DSC) tests were carried out using Netzsch DSC 214 Polyma (Netzsch, Germany), in order to determine the melting temperature (Tm) and the melting enthalpy (ΔHm) of PP within both fabrics (as fibres) and composites (as matrix). 15–20 mg of pure PP fibres were extracted from the commingled fabrics, and then heated from -40 to 220 °C at 10 °C/min in sealed aluminium pans. Nitrogen was used as a purge gas. Same tests were conducted on 15–20 mg samples cut from the composite laminates. The degree of crystallinity of PP within the fabrics and the biocomposites was calculated according to Equation 1:

$$X_c = \left(\frac{\Delta H_m}{\chi_m \times \Delta H^0{}_m}\right) \times 100 \quad \text{(Eq. 1)}$$

In Equation 1, χ_m and ΔH_m are the mass fraction (equals to 100% for pure PP fibres) and melting enthalpy of PP (calculated between 120 and 185 °C), respectively. $\Delta H^0{}_m$ is the melting enthalpy of a pure PP crystal, *i.e.* 207 J/g [22].

DSC tests were also performed on flax fibres extracted from the commingled fabrics. No drying procedure was applied to the fibres before running the DSC experiments.

The thermal stability of flax fibres was evaluated by thermo-gravimetric analysis (TGA). 15 mg of pure flax fibres were extracted from the fabrics. The change in mass versus temperature was measured from 30 °C to 800 °C with a heating rate of 20 °C/min in oxygen atmosphere. The kinetics of degradation of flax fibres for different isotherms was also studied by TGA. The thermal cycle applied to flax fibre samples was a two-step process: initial drying at 110 °C for 5 minutes followed by heating ramp to pre-defined temperatures (from 190 °C to 260 °C) and an isotherm stage of 14 minutes at that temperature, representative of the investigated processing conditions.

2.4. Mechanical properties of flax fibre yarns and fabrics

Flax fibre yarns and fabrics, also supplied by Composites Evolution without the commingled PP as Biotex Flax, were tested under uniaxial tensile loading. The tensile properties were measured using an Instron 5942 tensile test machine with a 500 N load cell. Flax fibre yarns of 100 mm length were tested at a constant crosshead displacement rate of 20 mm/min. Additionally, flax fabrics of 10 yarns in width were also tested in tension. In addition to sample drying at 70 °C to remove the moisture, the effect of thermal cycles on the mechanical behaviour of flax yarns and fabrics was studied by heating the samples in an oven at different temperatures (200, 220, 240 °C) for duration of 5 and 10 minutes, corresponding to typical processing temperatures and times. At least 10 samples were tested for each condition.

2.5. Microstructural analysis of flax / PP biocomposites

The overall fibre volume fraction v_f and porosity content v_p of the flax / PP composite laminates were calculated with Equations 2 and 3 from the density of the manufactured laminates ρ_c measured by gas pycnometry (Micromeritics AccuPyc 1330) in helium atmosphere after drying the samples minimum 2 hours at 70 °C. Measurements were done in triplicate. The density of PP matrix ρ_{PP} was taken as 0.905 g.cm^{-3}, the density of flax fibres ρ_f corresponds to the mean value of gas pycnometry measurements performed on dry flax fibres (ρ_f = 1.5204 g.cm^{-3}). The fibre weight loss

χ_d^f estimated from TGA data after 7 min or 12 min isotherms (corresponding to 2 min stabilization plus 5 min or 10 min of consolidation at a given temperature, respectively) was also considered in the calculations of ν_f and ν_p (Equations 4 and 5). In all these equations, χ_f refers to the mass fraction of fibres in dry commingled fabric that was assessed with Equation 6 from the initial flax fibre volume fraction of the fabric provided by the supplier (ν_{fi} = 0.4). For all processing conditions, PP flowing at the edges of the plates was very limited or not preponderant towards the squeezing of the fabrics. Consequently, variations in ν_f and ν_p are thus assumed to be only due to the formation of pores during processing and/or mass loss due to the degradation of the fibres.

$$\nu_f = \frac{\rho_c}{\rho_f}\chi_f \quad \text{(Eq. 2)}$$

$$\nu_p = 1 - \rho_c\left(\frac{\chi_f}{\rho_f} + \frac{1-\chi_f}{\rho_{PP}}\right) \quad \text{(Eq. 3)}$$

$$\nu_f = \frac{\rho_c}{\rho_f}\chi_f\left(1 - \chi_d^f\right) \quad \text{(Eq. 4)}$$

$$\nu_p = 1 - \rho_c\left(\frac{\chi_f\left(1-\chi_d^f\right)}{\rho_f} + \frac{1-\chi_f\left(1-\chi_d^f\right)}{\rho_{PP}}\right) \quad \text{(Eq. 5)}$$

$$\frac{1}{\chi_f} = 1 + \frac{\rho_{PP}}{\rho_f} \times \frac{1-\nu_{fi}}{\nu_{fi}} \quad \text{(Eq. 6)}$$

The microstructure of the flax / PP laminates manufactured at different processing conditions was observed across their thickness using a scanning electron microscope (SEM) (Quanta FEG 200, FEI Company). Samples were embedded in a clear epoxy resin and polished with progressively fine polishing papers. The polished cross sections were carbon coated and the acceleration voltage was set to 12.5 keV.

X-ray microtomography imaging experiments were conducted on selected samples to provide a comprehensive description of fibre and porosity volume distribution. Measurements were performed with an EasyTom XL from RX Solutions (France) to record 3D images of the microstructure of composites (voxel size: 3.3 × 3.3 × 3.3 µm³). The X-ray source was made of a LaB6 filament (cathode) and a W transmission target (anode), and had an accelerating voltage of 40 kV. A CCD

detector of 2048 × 2048 pixels from Princeton Instruments (USA) was used. The samples were cut from the different plates to get a size of approximately 5 × 5 mm². They were placed horizontally in the equipment such as the X-ray beam was always orthogonal to their thickness during scanning. For each processing conditions, materials were tested in duplicate. The scans were reconstructed using the X-Act CT software and then segmented with the ImageJ software [23]. Segmentation was achieved using the Trainable Weka Segmentation 3D plugin [24]. The volume fibre content and the porosity were defined as the ratio of the number of voxels corresponding to the volume of fibres and pores, respectively, over the total amount number of voxels in the cropped region. Pore volumes were assessed with the BoneJ particle analyser and sorted in classes in order to evaluate their distribution [25].

2.6. Uniaxial tensile testing on flax / PP biocomposites

A Zwick Z010 testing machine was used to perform tensile tests based on the ISO 527-4 standard for composites. The width and thickness of each sample was measured before every test and the length between the fixing jaws was 110 mm (length of actual samples: 165 mm). Five samples were tested per processing condition and each test was conducted in two stages: a first stage at a crosshead speed of 1 mm/min using an extensometer to determine the tensile modulus (calculated by considering the slope of a linear trendline of the stress-strain curve between a strain of 0.05% and 0.3%), and a second stage at a crosshead speed of 5 mm/min until rupture to determine the tensile strength and strain at break. The tests were conducted in a controlled environment (ca. two hours at temperature of 25 °C and 50% relative humidity).

3. Results and discussion

3.1. Thermal behaviour of polypropylene and flax fibres

The typical heat flow results of the DSC analysis performed on flax and PP fibres extracted from the flax / PP commingled fabric are shown in Figure 2. It can be seen from the heat flow curves of the first heating cycle that the endothermic melting peak of PP fibres is at 168.8 °C. The melting enthalpy ΔH_m calculated from the area under the melting curve of pure PP was found to be 91.4 J/g, which corresponds to a degree of crystallinity of 44.2% as calculated according to Eq. 1. DSC curve of flax fibres exhibits a large endothermic peak around 110 °C primarily attributed to the evaporation of residual moisture in flax fibres.

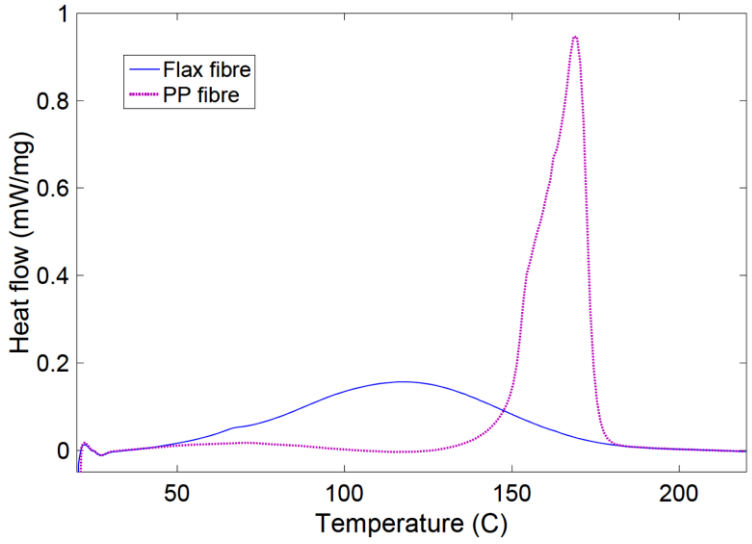

Figure 2. DSC heating scan for the first heating cycle of PP fibres and flax fibres.

The thermal stability of flax fibres was evaluated using thermo-gravimetric analysis (TGA). The change in mass versus temperature was measured and is shown in Figure 3a. Three peaks associated to weight losses are generally observed in the derivative TGA curves of flax fibres. The first mass loss with peak at 98.8 °C is related to the release of water. The second peak at 200 °C which can be seen as a shoulder on the main peak is related to the degradation of low molecular weight and non-cellulosic substances such as hemicelluloses (especially xylan in the case of flax),

pectins and waxes [26]. The third and main peak is associated to the degradation of cellulose which occurs at 356 °C for the flax fabric selected in this study. It should be pointed out that the degradation of lignin generally occurs over a wide temperature range, *i.e.* from 200 to 500 °C [26,27]. The decomposition peak of PP matrix has been measured at 416 °C (Figure 3a), hence at much higher temperature than the starting degradation temperature of flax fibres.

Exposure time to high temperatures is also critical and the kinetics of thermal degradation of flax fibre for different isotherms (after prior drying at 110 °C) is shown in Figure 3b. It can be observed significant variations in mass loss over time and the extent of degradation increases drastically with increasing isothermal temperatures. After 10 minutes, flax fibres lost about 2.0% mass when heated at 220 °C, while mass losses reached 3.6 and 6.0% at 240 °C and 260 °C, respectively.

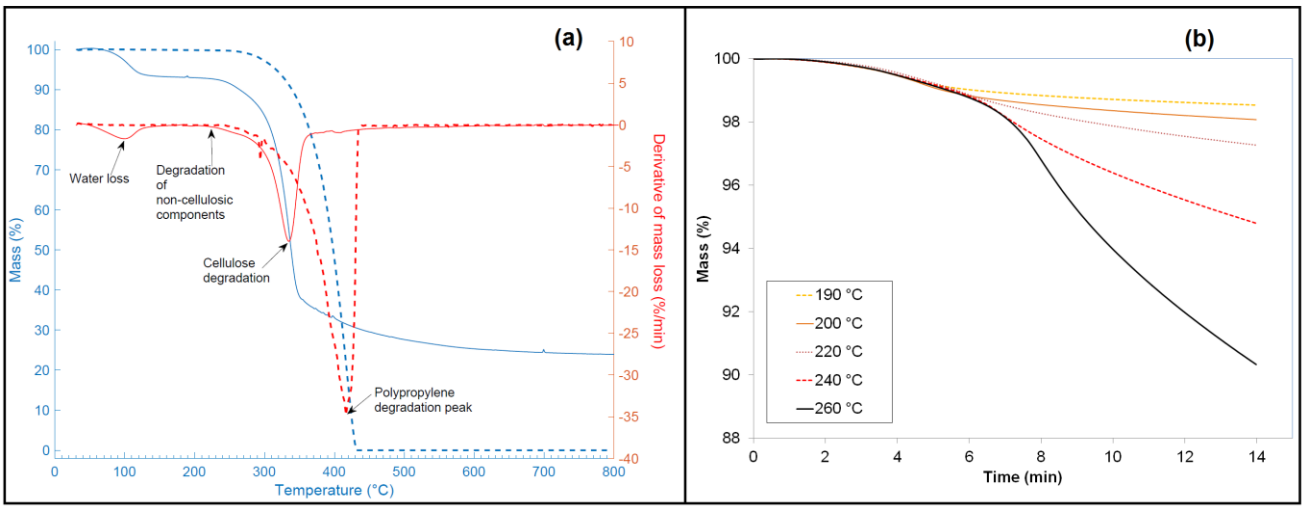

Figure 3. (a) TGA curves for flax fibres (solid lines) and PP (dashed lines) highlighting the main mass loses and degradation peaks, (b) kinetics of thermal degradation of flax fibres at different isothermal temperatures.

Based on the biochemical composition analysis (see section 2.1), flax fibres used contain almost 80% of cellulose and 20% of non-cellulosic components, *i.e.* lignin, hemicelluloses, and low molecular weight soluble. The mass losses recorded after exposure 10 min at 240°C and 260°C (*i.e.*

3.6 and 6.0%) clearly highlight that a large part of the non-cellulosic components (and possibly small amount of cellulose) were degraded over short exposure times. These non-cellulosic components play a key role in the intra and inter-cellular cohesion and transfer loading mechanisms within flax fibre bundles [28–30], and such extensive degradation should thus have a great influence on the resulting mechanical properties of flax fabrics and flax / PP composites.

The thermal stability study was completed by tensile tests performed on flax yarns and fabrics heated at various temperatures. Dried flax yarns exhibited large variations in their mechanical behaviour. The stiffness and overall mechanical response were highly variable (see supplementary data S1). It was observed that some yarns show damage initiation at small displacements but the elementary fibres and/or fibre bundles continued to withstand the load until full rupture. Considering the tested yarn length (*i.e.* 100 mm), sliding between the twisted fibres also occurred. For some tests, the failure in the yarns was more brittle and a sharp drop in the force can be seen. The peak force varied from 15.7 N to 35.8 N while the maximum displacement at rupture also varied from 8.6 mm to 14.3 mm. It was not possible to identify a pattern in the mechanical response of the flax yarns after the heating cycles due to this large scattering in mechanical behaviour. Nevertheless, it was possible to observe tendencies on the flax fabrics made of ten yarns and tested in the longitudinal direction. It can be observed in Figure 4, that increasing the isothermal temperature reduces drastically the stiffness and the peak force of the fabric, attesting that the thermal degradation of the non-cellulosic components measured by TGA has a pronounced effect on the mechanical response of the flax fabrics. Exposure to temperatures higher than 200 °C turned out to be detrimental for the mechanical performances of flax fibre fabrics, mainly due to early breakage of elementary fibres within the yarns. According to Bourmaud et al. [9], exposure to higher temperatures lead to significant modification of the flax fibres such as its biochemical composition and macromolecular arrangement. These modifications affect the sliding of cellulose microfibrils within the cell walls, and therefore lead to a decrease of Young's modulus and strength of the fibres. Van de Velde and

Baetens [8] showed that the removal of water occurring at 120 °C makes the fibre more brittle. Indeed, water acts as plasticizer in the fibre microstructure. Degradation of pectins at around 180 °C, which are mostly present in the middle lamella and hold the elementary fibres together, had a faster and detrimental effect on the mechanical properties of the green and under-retted fibres.

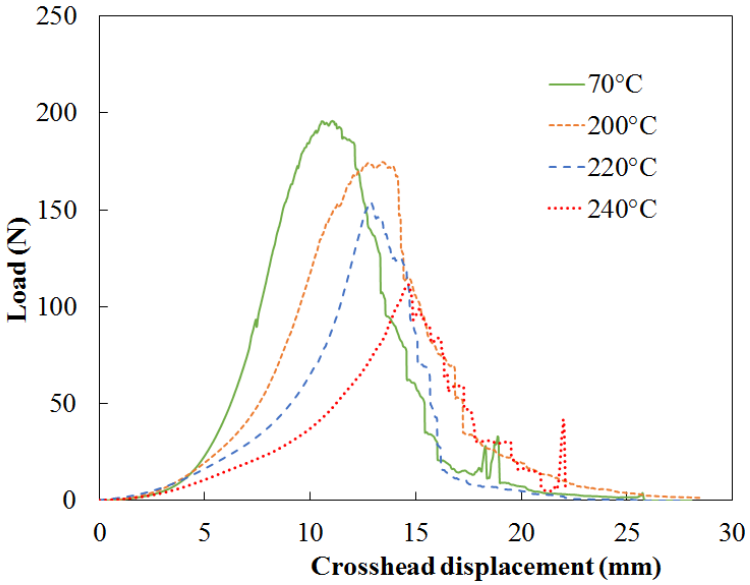

Figure 4. Force – displacement curves for flax fabrics made of ten yarns and exposed at different temperatures for 10 min.

3.2. Choice and monitoring of processing conditions for the manufacturing of flax / PP biocomposites

The processing conditions for the flax / PP composite were chosen based on the results of the thermal analysis of individual constituents. The chosen processing temperature window should be sufficiently high so as to completely melt and flow the PP matrix. Indeed, at higher temperatures, the PP viscosity decreases allowing a better flow and possibly better impregnation within the flax yarns. However, as previously discussed, too high temperatures could degrade drastically flax fibre structure and its resulting mechanical performances. Based on our results, 17 composite laminates were manufactured with contrasted processing parameters so as to highlight the effect of manufacturing conditions on the microstructure and mechanical behaviour of flax / PP composites

when using the induction-heated press. The chosen processing parameters, *i.e.* temperature, pressure and consolidation time used are summarised in Table 1. The nomenclature for the samples follows the rule **xC_ym_zb**, with x corresponding to the temperature in °C, y to the consolidation time in minutes and z the pressure in bars.

Table 1. Summary of the processing conditions used for the manufacturing of flax / PP composite laminates.

Plate n°	Temperature (°C)	Time (min)	Pressure (bar)	Plate_name
1	190	10	20	190C_10m_20b
2	190	10	40	190C_10m_40b
3	200	5	20	200C_5m_20b
4	200	5	40	200C_5m_40b
5	200	10	20	200C_10m_20b
6	200	10	40	200C_10m_40b
7	220	5	10	220C_5m_10b
8	220	5	20	220C_5m_20b
9	220	5	40	220C_5m_40b
10	220	5	40	220C_5m_40b (slow)
11	220	5	40	220C_5m_40b (Fast)
12	220	10	20	220C_10m_20b
13	220	10	40	220C_10m_40b
14	240	5	20	240C_5m_20b
15	240	5	40	240C_5m_40b
16	240	10	40	240C_10m_40b
17	260	5	20	260C_5m_20b

The induction-heated press allowed to continuously monitor the actual temperature, the pressure applied, and the platen position during processing. A typical processing cycle for the manufacturing of a flax / PP composite at 200 °C is shown in Figure 5. Maximum heating power was applied for the heating phase (phase 1) and the heating rate was roughly 40 °C/min for all the experiments. When the targeted processing temperature was reached, a stabilization time of 2 minutes was allowed (phase 2) before applying the pressure and starting the clock to measure the consolidation time (phase 3). It is interesting to note that the position of the upper plate was

decreasing in the first minutes of the consolidation due to PP flowing, hence decreasing the thickness of the laminate. At the end of the consolidation phase, the cooling system was turned on (phase 4) and the temperature was allowed to decrease rapidly until 140 °C. The cooling rate was then reduced at this temperature to aid the crystallisation of the PP matrix and then increased back to reach ambient temperature. The effect of a slow and fast cooling cycle (plates n°10 and 11) was also tested with cooling rates of 2 °C/min and 25 °C/min, respectively. It should be pointed out that for all the experiments a constant pressure was maintained during the entire consolidation and cooling phases. It must also be noticed that from the moment a constant pressure is applied, the displacement of the press platen is related to the thermal expansion of the mould and material, and to the thickness reduction of flax / PP composite laminate. The consolidation process can therefore be monitored during the isotherm by the decreasing position of the upper plate. As it can be observed, the thickness reduction occurs during the first minutes of the isotherm stage, which indicates that the consolidation of flax / PP composite laminate is almost entirely achieved within five minutes after the application of the pressure.

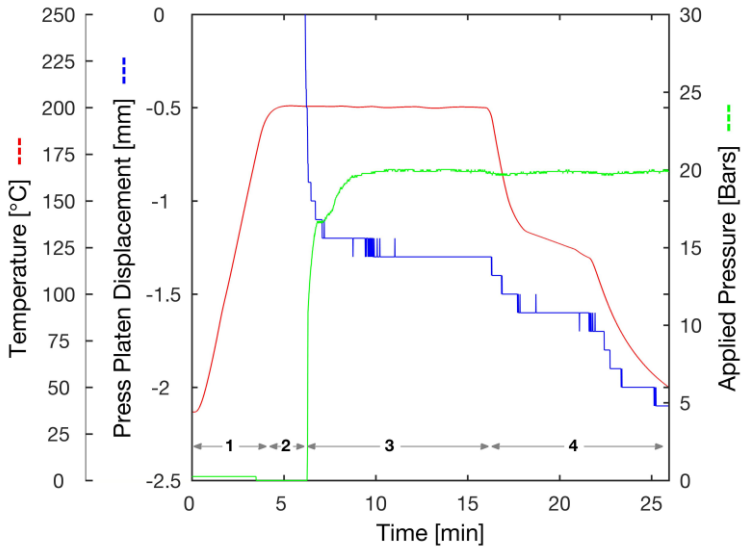

Figure 5. Typical processing cycle: measured temperature, pressure and platen position over the whole manufacturing process. Phase 1 (heating), phase 2 (stabilization), phase 3 (consolidation under pressure) and phase 4 (cooling).

It is worth mentioning that the composites manufactured at 240 °C during 10 minutes and 260 °C during 5 minutes were completely destroyed due to the thermal degradation of the fibres. The resulting composite laminates were unusable and not characterized. The images of the resulting composite laminates are shown in supplementary data (S2).

3.3. Microstructural analysis of flax / PP biocomposites

The effect of the processing conditions on the crystallisation of PP matrix was investigated with DSC tests performed on the different manufactured composite laminates. The thermograms were very similar for the different manufacturing conditions (see supplementary data S3). Melting peak temperature was not influenced by the processing conditions, roughly 167 °C for all the plates, attesting that the crystals formed upon cooling had the same thermal stability and melted in the same temperature range. In the same cooling conditions, melting enthalpy and degree of crystallinity varied from 46.1 to 53.4 J/g, and 47.2 to 54.7% (Table 2), respectively. Although DSC tests were achieved on several samples for each plate, it must be noted that the actual fibre weight within the DSC samples could not be perfectly controlled. For this reason, in overall, the variations of the degree of crystallinity cannot be considered significant, and it can be assumed that it was not influenced by the processing conditions. However, the effect of cooling rate on the crystallization of PP was the most influential. For fixed processing conditions (220 °C, 40 bar, 5 min), slow cooling cycle promotes higher degree of crystallinity, *i.e.* 55.0 % instead of 46.4 % for the fast cooling cycle (Table 2). A secondary melting peak or shoulder at 150 °C was visible in some processing conditions. This may be attributed to the presence of beta phase crystal which formation could be favoured by higher consolidation pressure, *i.e.* 40 bar, during crystallization [31].

The estimated overall fibre volume fraction and porosity calculated from pycnometry measurements with Equation 2 and 3 (without accounting for fibre degradation) and Equations 4 and 5 (accounting for fibre degradation) are presented in Table 2 for the different processing conditions. It can be observed that the different processing conditions had a limited effect on the fibre volume

fraction ranging between 37.7 and 39.6% depending on the processing parameters and calculation method (*i.e.* with or without accounting for fibre degradation). An increase in operating pressure from 20 bar to 40 bar slightly improved the fibre volume fraction of about 1 % for the lowest processing temperatures (≤ 200 °C). The processing temperature had no significant effect on the fibre volume fraction, being in average 39.1 %, 38.8 % and 39.1 % (without accounting for fibre degradation) and 38.6 %, 38.1 % and 38.4 % (accounting for fibre degradation) for 200 °C, 220 °C and 240 °C, respectively.

Table 2. Biocomposite densities, fibre volume fraction, porosity, melting enthalpy and degree of crystallinity of manufactured flax / PP composites laminates.

Plate_name	**Composite density ρ_c** [a]	**Fibre volume fraction v_f (%)** (without fibre degradation, Eq. 2)	**Porosity v_p (%)** (without fibre degradation, Eq. 3)	**Fibre volume fraction v_f (%)** (with fibre degradation, Eq. 4)	**Porosity v_p (%)** (with fibre degradation, Eq. 5)	**Melting enthalpy ΔH_m (J/g)** [b]	**Degree of crystallinity X_c (%)** [c]
190C_10m_20b	1.124	39.0	2.4	38.5	2.0	50.3	51.5
190C_10m_40b	1.139	39.6	1.1	39.0	0.7	51.2	52.5
200C_5m_20b	1.113	38.7	3.3	38.1	3.0	48.4	49.5
200C_5m_40b	1.137	39.5	1.3	39.0	0.9	46.1	47.2
200C_10m_20b	1.107	38.5	3.9	37.8	3.4	49.3	50.5
200C_10m_40b	1.139	39.6	1.1	38.9	0.6	49.1	50.2
220C_5m_10b	1.123	39.0	2.4	38.5	2.0	48.1	49.3
220C_5m_20b	1.111	38.6	3.5	38.1	3.1	47.9	49.1
220C_5m_40b	1.128	39.2	2.1	38.6	1.7	48.9	50.0
220C_5m_40b (slow)	1.136	39.5	1.3	38.9	0.9	53.8	55.0
220C_5m_40b (fast)	1.121	39.0	2.6	38.4	2.2	45.3	46.4
220C_10m_20b	1.111	38.6	3.5	37.7	2.8	53.4	54.7
220C_10m_40b	1.116	38.8	3.1	37.8	2.4	46.1	47.2
240C_5m_20b	1.126	39.1	2.2	38.4	1.7	47.2	48.4
240C_5m_40b	1.125	39.1	2.3	38.4	1.8	47.5	48.6

[a] Average STD: 0.0028; [b] Average STD: 2.16; [c] Average STD: 2.68

Figure 6 shows a 3D interpolated plot of the calculated porosity as function of the consolidation temperature, pressure and time. A porosity fraction lower than 3.9 % (3.4 % when accounting for fibre degradation) was obtained for all conditions with a minimum porosity fraction

of 1.1 % (0.6 % when accounting for fibre degradation) observed for processing at 200 °C under 40 bar during 10 min. Those relatively low values of overall porosity may be attributed to the thorough mixing between the flax and PP fibres inside the commingled yarns [13,14,16], and the resulting good impregnation during manufacturing. Figure 6a shows that consolidation time has little effect on porosity. In contrast, depending on the processing temperature, a decrease in the overall porosity of up to 2-3 % can be observed when increasing pressure. The processing temperature also appears to be a very influential parameter that affected the final composite porosity (Figure 6b). However, increasing temperature did not result in a progressive reduction of porosity as it could be expected regarding the temperature-dependent behaviour of PP viscosity and flowing. Maximum porosity was reached at intermediate processing temperature, *i.e.* between 200 and 220 °C. This represents a significant difference with synthetic fibres commingled fabrics for which increasing temperature has a positive effect and results in a decrease of overall porosity due to better matrix flowing and improved fibre impregnation [15]. According to Pickering et al. [4] and Madsen et al. [32], fibre lumens and other inaccessible regions within elementary fibres and/or fibre bundles as well as the limited wettability of natural fibres towards apolar and viscous matrices such as PP, lead to poor impregnation and inclusion of air bubbles during processing and the formation of micro and macro-pores. Besides, it has been shown by Madsen et al. [33] that porosity in natural fibre reinforced composites could even increase at high fibre content, if the geometrical compaction limit is reached, due to limited packing ability of natural fibres.

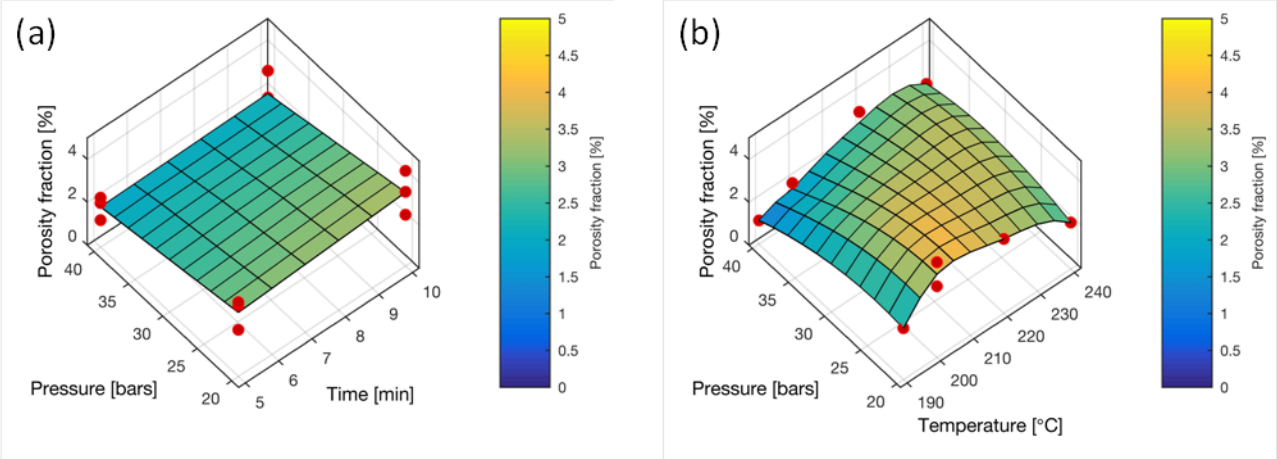

Figure 6. Overall porosity based on pycnometry measurements (without accounting for fibre degradation, Eq. 3) of flax / PP composite laminates for different processing conditions: (a) pressure vs. time, (b) pressure vs. temperature.

Cross-sectional microstructures of flax / PP composite laminates manufactured in contrasted processing conditions are shown in Figure 7. Both warp and weft fibre yarns of the different plies are visible in the cross-section of the plate (Figure 7a and d). As reported by Madsen et al. [32], different kinds of pores are visible within the composite microstructure including macro-pores which are typically caused by *(i)* entrapped gas bubbles or voids within the matrix, and micro-pores originating from *(ii)* natural fibres themselves, *(iii)* interfacial pores and *(iiii)* bad impregnation within the yarns. At higher magnification (within the flax yarns), interfacial pores in between the elementary flax fibres and the matrix are observed (see arrow), suggesting poor interfacial adhesion (Figure 7c and f). For the composite processed at higher temperature, *i.e.* 240 °C, higher degree of individualization of the elementary fibres (Figure 7e compared to 7b) can be observed. However, the lumen (central channel) of the elementary fibres shows several micro-cracks (Figure 7f) supporting the hypothesis of a thermal degradation of flax fibres and their destructuration at high operating pressure and temperature.

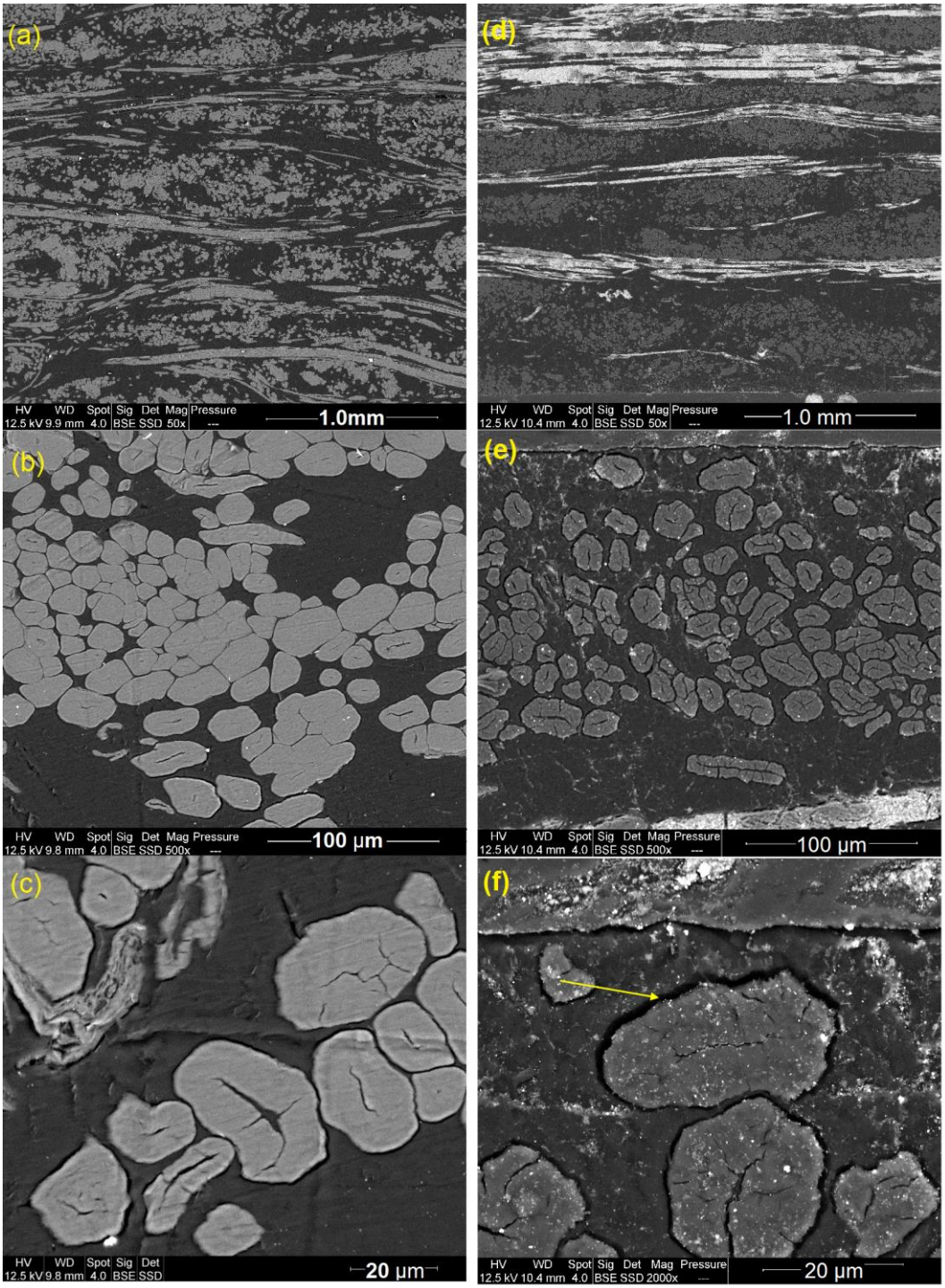

Figure 7. Microstructure in cross-sections of flax / PP composites as observed by SEM for: 190C_10m_40b (a, b, c); and 240C_5m_40b (d, e, f) laminates.

Based on these observations, we postulated that pores might also originate from the release of volatiles during processing resulting from the thermal degradation of flax fibres. In this regard, X-ray tomography experiments were conducted to investigate the local porosity volume distribution within

the samples and better depict the influence of the processing temperature, time and pressure on porosity. Figure 8 shows the 3D images of pores in selected composites. The porosity volume fraction calculated from tomography confirms that the operating pressure and temperature have a great influence on the formation of pores. At 200 °C, increasing the pressure from 20 bar to 40 bar had a drastic effect on the local porosity (Figure 8a and b) that decreased from 1.81 ± 0.41 % to 0.23 ± 0.05 %. Increasing the temperature from 200 °C to 240 °C at constant pressure (40 bar) increased the local porosity (Figure 8c), i.e. 0.78 ± 0.01 %, confirming the results in Table 2. It is also interesting to note that slowing down the cooling rate increases the local porosity up to 1.37 ± 0.01 % (Figure 8d), which suggests that longer processing time could also influence the formation of pores.

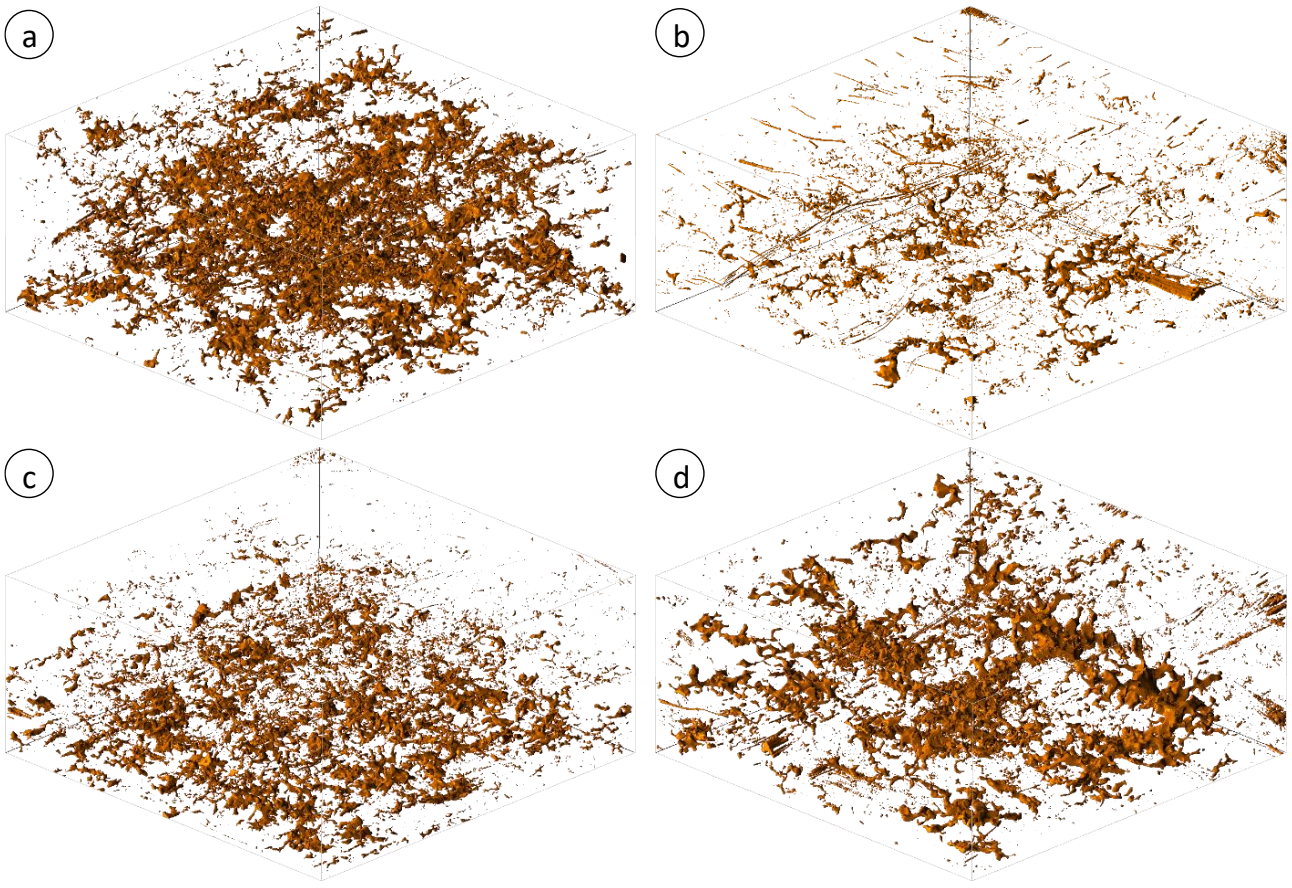

Figure 8. 3D images of pores in flax / PP composite samples (3800 × 3800 × 1650 µm^3) obtained by X-ray tomography experiments for: (a) 200C_5m_20b; (b) 200C_5m_40b; (c) 240C_5m_40b and (d) 220C_5m_40b (slow).

X-ray tomography measurements also give access to the analysis of the distribution of pore volumes (Figure 9). A clear tendency toward the diminution of the pore size was observed when increasing the operating pressure (200C_5m_20b compared to 200C_5m_40b). This supports the hypothesis that higher pressure favours matrix flowing and fibre impregnation, hence limiting the formation of micro-pores (so called impregnation porosity) within the yarns. Interfacial pores remained due to poor adhesion between PP and flax. In contrast, higher processing temperature and time (240C_5m_40b and 220C_5m_40b (slow)) resulted in the formation of macro-pores between the yarns. This supports the hypothesis that volatiles are formed during processing by the thermal degradation of flax fibres and partially entrapped within the viscous matrix.

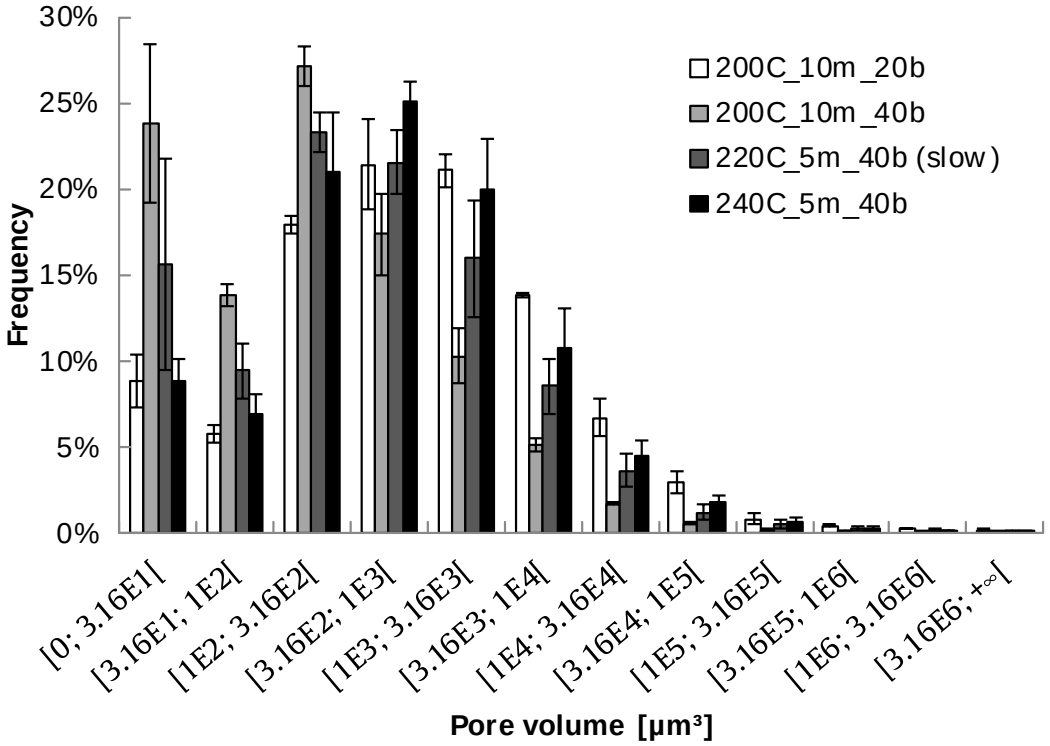

Figure 9. Pore volume distribution weighted in volume for: 200C_10m_20b; 200C_10m_40b; 240C_5m_40b and 220C_5m_40b (slow).

Concluding, it has been demonstrated that the processing parameters, *i.e.* consolidation time, pressure, temperature and cooling rate, have counterbalancing effects on the development of microstructures in commingled flax / PP biocomposites:

- Increasing pressure, temperature and processing time (consolidation and cooling) favours matrix flowing and fibre impregnation, leading to lower porosity and smaller pores, and enhancing crystallization.
- But too high processing temperature and time can cause the thermal degradation of the fibres that leads to the formation of volatiles and thereby macro-pores.

In the following, these balanced effects of processing conditions were studied as regard the mechanical behaviour in the elastic domain and at rupture. From the microstructural analysis, it can be assumed that the mechanical behaviour of the composites is mainly affected by the extent of degradation of flax fibres, and the type of developed pores either interfacial micro-pores or macro-pores in the bulk of the matrix.

3.4. Uniaxial tensile behaviour of flax / PP biocomposite

Figure 10 compares the stress-strain curves of composites manufactured at different temperatures. All composite materials exhibit a similar behaviour, with a quasi-linear elastic domain up to 0.5-0.8% strain until reaching an inflection point (yield point). This inflection point should be related to the viscoplastic behaviour of PP and/or the beginning of damage within the composite structure, *i.e.* micro-cracks at the interface and within the matrix, which finally leads to the critical fracture of the specimens. The exposure to high processing temperature during composite manufacturing induced a more brittle behaviour, which consequently also resulted in a reduction of composite strength. The median strength and strain at failure indeed decreased from 79.1 MPa to 52.9 MPa and from 2.1% to 1.0%, respectively, when increasing the processing temperature from 190 °C to 240 °C.

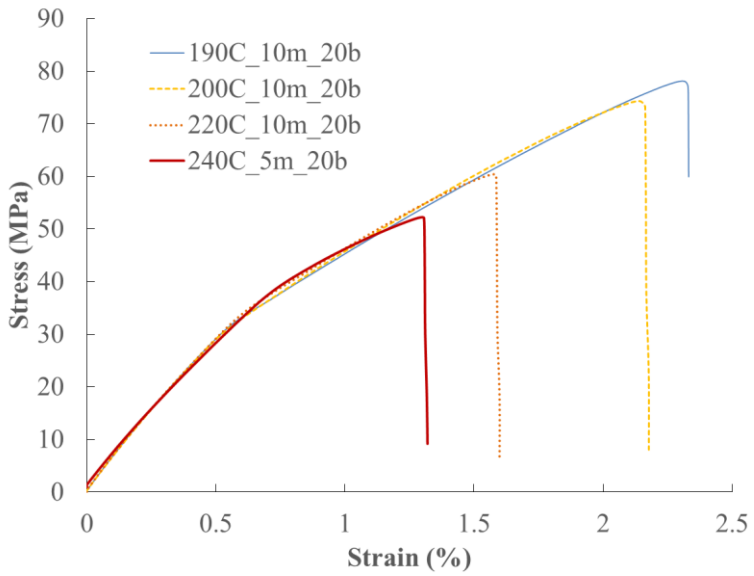

Figure 10. Comparison of stress strain curves for different processing temperatures

In order to analyse the effects of manufacturing conditions on the mechanical properties of flax / PP biocomposites, the Young's modulus and strength were recorded for all conditions and data were interpolated so as to highlight the combined effects of temperature, pressure and consolidation time (Figure 11).

It can be seen that the pressure had a pronounced positive effect on the Young's modulus (Figure 11a), higher consolidation pressure being associated to higher modulus, *i.e.* up to 1 GPa increase from 20 bar to 40 bar. In contrast, pressure had little to no effect on composites strength (Figure 11b). Based on the microstructural analysis, we assume that the higher Young's moduli obtained with higher pressure are due to better flax fabrics impregnation inducing higher fibre volume fraction, better fibre individualization, and fewer and smaller pores (Table 2 and Figures 8 and 9). It should be noticed that the effect of pressure was somewhat less pronounced at 240 °C. In this case, a high modulus was obtained for both 20 and 40 bar due to better flowing of the matrix and hence better impregnation of the fabrics.

On the other hand, the combined effect of temperature and consolidation time are presented in Figure 11 (c, d), and it can be seen that the effect of higher temperature and longer time was

detrimental for the strength of the composites, which reduced drastically to 52.9 MPa at 240 °C. As discussed above, the drastic decrease of intrinsic mechanical properties of the fibres (Figure 4) associated to damages within their microstructure (Figure 7) is responsible for the severe degradation of the ultimate performances of the biocomposites. Furthermore, the development of macro-pores (Figure 8 and 9), related to fibre degradation and consecutive entrapping of volatiles in the bulk of the matrix, induces numerous macro-pores that greatly amplify the ultimate performance losses. It is interesting to note that high modulus of the composites could be maintained even when processed at 240 °C for 5 min consolidation (Figure 11a and c). Thermal degradation of the fibres and formation of macro-pores in these processing conditions is thus not detrimental to the stiffness of the composite.

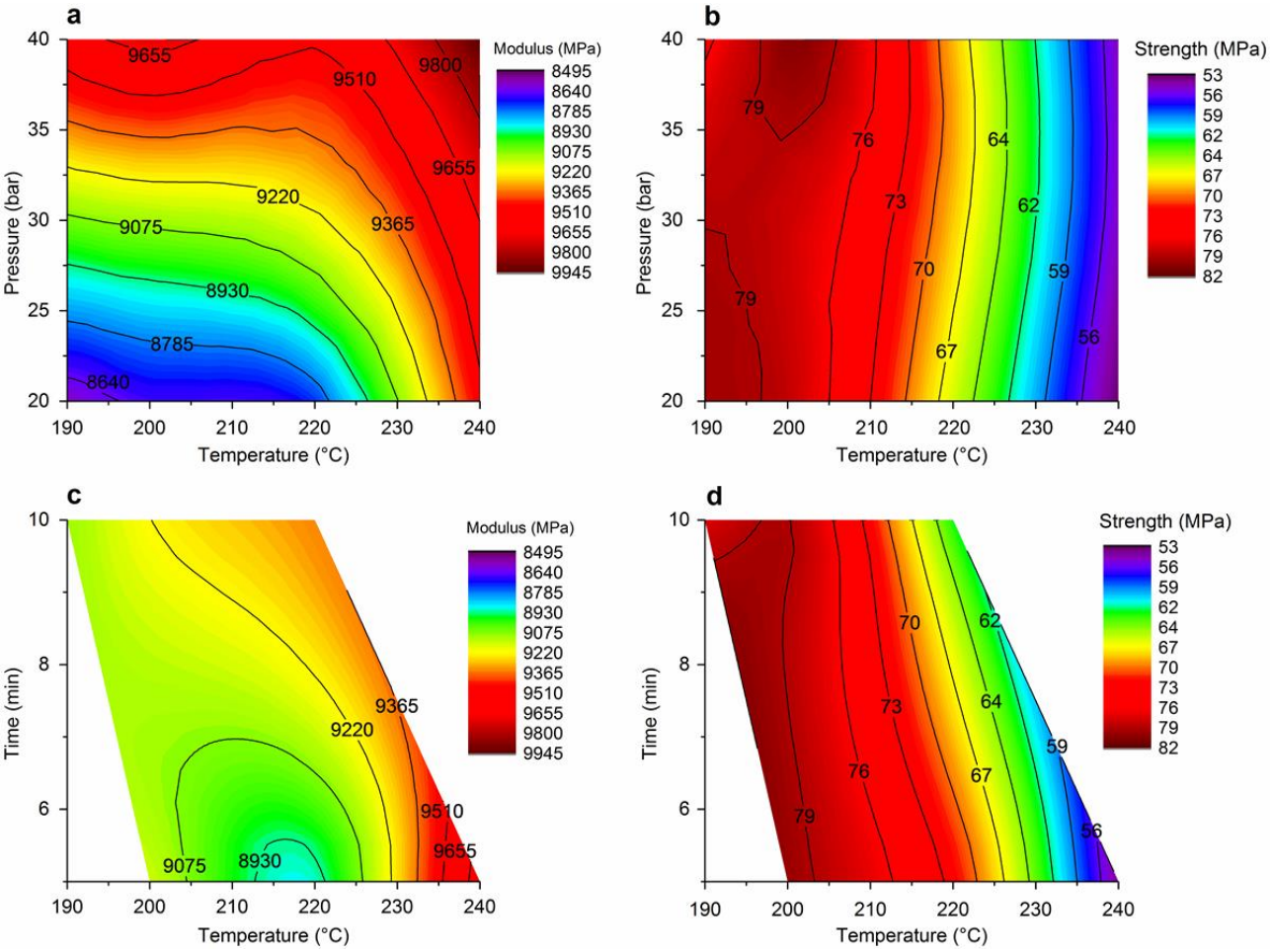

Figure 11. (a, b) Effect of temperature and pressure and (c, d) effect of temperature and consolidation time on median modulus and strength of flax / PP biocomposites.

Finally, the effect of the three cooling cycles on the modulus and strength of the flax / PP composite is shown in Figure 12. It can be seen that there is no appreciable difference between the fast and optimal cooling condition, while there is a substantial drop in both the modulus and strength for the slow cooling. This shows that when flax fibres are exposed to high temperature for prolonged duration due to slow cooling cycle, thermal degradation and its related consequences on the formation of macro-pores and degradation of fibres, are most likely to occur.

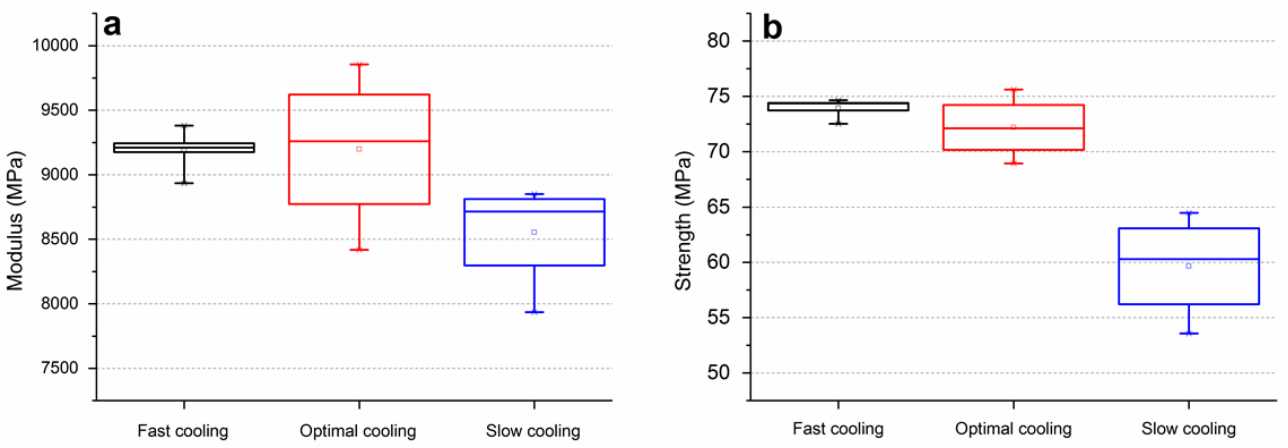

Figure 12. Effect of cooling cycle on (a) modulus and (b) strength for flax / PP composite manufactured at 220 °C for 5 min under 40 bar.

4. Conclusions

In this study, lightweight thermoplastic biocomposites from commingled flax / PP fabrics were manufactured using a fast induction-heated compression moulding system. The thermal behaviours of flax and PP fibres were evaluated by DSC and TGA analysis. Various and contrasted processing conditions were selected to study their effect on the microstructure development and the mechanical behaviour of the biocomposites. Based on a careful microstructural analysis of the biocomposites through DSC, pycnometry, SEM and X-ray tomography, the balanced effects of processing conditions were identified and described: (*i*) increasing pressure, temperature and processing time (consolidation and cooling) favours matrix flowing and fibre impregnation, leading to fewer and smaller pores, and enhanced crystallization; (*ii*) but too high processing temperature and time can

cause the thermal degradation of the fibres, leading to the formation of volatiles and thereby macro-pores. The detailed description of the microstructure allowed depicting the processing / microstructure / mechanical behaviour relationships of the manufactured flax fibres / PP biocomposites. Elastic properties of the biocomposites could be maintained even at high processing temperature (240 °C for 5 min of consolidation appearing as the upper limit), but their strength was drastically decreased due to extensive fibre degradation and formation of macro-pores. The use of fast processing tools as induction-heated systems can thus be interesting solutions to overcome the thermal degradation processes occurring with natural fibres reinforced biocomposites. Indeed, an optimised set of processing parameters can be chosen that would allow improvement of the microstructure with limited porosity and fibre degradation. These results open interesting perspectives for the use of higher melting point matrices and the production of biocomposites with higher mechanical performances. Efficient flowing of the matrix for optimal impregnation of natural fibres fabrics remains a key issue.

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Appendix A. Supplementary material.

Supplementary data associated with this article can be found, in the online version, at XXXX

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